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Impact of shallowly deposited ore-bearing dolomites on local soil pollution aureoles of As, Cd, Pb, and Zn in an old mining area

Piotr Fabijańczyk · Jarosław Zawadzki

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Abstract
Purpose The study area, located in Upper Silesian Industrial Region, was rich in significant amounts of ores that were classified of Mississippi Valley type. Being these ores especially rich in Pb and Zn, an intense development of mining and ore extraction industry was verified in this area. The goal of this study was to investigate how local pollution aureoles of As, Cd, Pb, and Zn were influenced by the presence of shallowly deposited ore-bearing dolomites.
Materials and methods Very extensive sampling campaign was carried out, and over 1,000 samples were collected in the area of about 150 km^2. Local aureoles of investigated metals were calculated for two soil layers. The first one covered the part of soil core from the soil surface to the depth of 20 cm and the second one from the depth of 40 cm to the depth of 60 cm. All spatial distributions of particular metals in soil were calculated by means of ordinary kriging using free softwares QGIS and SAGA.
Results and discussion Maximum concentrations of Pb and Zn in soil in study area were very high, reaching over 24,000 and 77,000 mg/kg, respectively. Maximum concentrations of As and Cd were also very high, reaching about 1,000 mg/kg. Those maximum values were observed in the direct vicinity of the Bolesław mine and its mine dumps. Almost all local aureoles were located within the range of ore-bearing dolomites. It was especially visible for Pb and Zn, minerals very common in ore deposits. Otherwise, local aureoles of As and Cd were more related with the vicinity of mines and other pollution sources, being more associated to the anthropogenic pollution than to the presence of ore-bearing dolomites.
Conclusions The aureoles of Pb and Zn, and in moderate degree of As, were associated with a mineral composition of ores. Differently, the location, the shape, and spatial pattern of Cd aureoles suggest that they were mostly influenced by anthropogenic pollution. Anthropogenic factors were dominating over the lithogenic ones and masking the influence of the shallowly deposited ores.

Keywords As · Cd, Pb, and Zn in soil · Mining area · Ore-rich dolomites · Pb–Zn ores · Pollution aureoles

1 Introduction

Areas of mining and steelworks are subjected to the major sources of pollution mainly for Pb and Zn that are accumulated in the top 10 cm of soil layer (Lee and Kao 2004; Ettler et al. 2004). Heavy metals accumulated in soil were gradually dispersed in the soil profile, and this process depends on the pH, soil type, water content, carbonates present in soil, and other factors. As it was found by Miller and Friedman (1994), the average speed of dispersion through the soil profile can reach about 0.5 cm/year and in case of forest soils even up to 2 cm/year.

Studies carried out so far in the study area, located in Upper Silesian Industrial Region (USIR), Poland, confirmed that this region is rich in Zn and Pb ores which occurrence was strictly connected to the presence of ore-rich dolomites. Consecutively, the very intense mining activity, deployment of the mining wastes, and complex geology were the causes of the creation of local dispersion aureoles of Zn and Pb (Cabała 2009; Mayer et al. 2001). These aureoles were observed in the vicinity of the geological faults and in areas with the presence of ore-rich dolomites. In such areas,

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P. Fabijańczyk (✉) · J. Zawadzki
Environmental Engineering Faculty,
Warsaw University of Technology,
Nowowiejska 20,
00-653 Warsaw, Poland
e-mail: p.fabijanczyk@gmail.com

shallowly deposited ores were directly exposed to the hypergenic factors. In consequence, aureoles were observed not only in the bedrock, but also in soil.

If most of the heavy metals are present in high concentrations in the topsoil layer, it can be assumed that they are of anthropogenic origin (Hanesch and Scholger 2005; Magiera et al. 2006). However, in mining areas, especially those characterized by the presence of deposited ores, aureoles of heightened concentration of Pb and Zn can be also a result of shallowly deployed ore-bearing dolomites (Mayer et al. 2001). Consequently, the discrimination between the lithogenic and anthropogenic origin of Zn and Pb aureoles in old mining areas, which is a primary important problem, can very complex and difficult. It may be also difficult when measurements will be carried out only on one depth in soil profile. In consequence, it may be difficult to monitor soil pollution in such type of areas, especially using supplementary measurement techniques.

The goal of this study was to investigate how local aureoles of As, Cd, Pb, and Zn were influenced by the presence of ore-bearing dolomites that were deposited shallowly beneath the soil surface. Very extensive sampling campaign was carried out, covering over 1,000 sample points. Moreover, at each sample point, collected soil cores were used to determine the content of As, Cd, Pb, and Zn on two layers in soil profile. Local aureoles of investigated metals were calculated and their locations were related to the geological conditions, in specific the presence of ore-bearing dolomites.

2 Study area

2.1 Location of the study area

The study area was located in USIR, placed mostly in Silesian Voivodeship in Southern Poland. USIR covered over 3,000 km^2 and has high number of coal mines, power plants, and steelworks, being one of the most industrialized areas in Europe. The center of the USIR was occupied by Katowice urban area, which is one of the most populated areas in Poland (over two million).

The study area was almost square-shaped and of about 150 km^2. In this region, the largest residential territory, Sławków town, is located at the western edge of the study area (Fig. 1). The most important pollution sources were located in the eastern part of the study area, including Bolesław mine and its large mine waste dump. The remaining part of the study area was mostly occupied by forest (the northeastern part) and open areas (the central part).

2.2 Historical background of ore exploration

Significant amounts of shallow ore deposits located below the soil surface initiated rapid development of the ore extraction industry in the study area. The beginning of the mining, focused on the extraction of mostly Ag, Pb, and Zn, was dated at twelfth century, while the significant intensification of mining was observed in eighteenth and nineteenth century due to the new mining and extraction technologies. At the end of nineteenth and the beginning of twentieth century, the extraction of Zn ores was one of the highest in the world. In mid-1970s, the extraction of Zn reached over 200,000 tons. During this period, numerous mines, opencast mines, were built and the entire area was strongly industrialized.

Long history of ore extraction has resulted in substantial amounts of wastes, rich in particular in Zn and Pb, that were produced and deposited on the soil surface (Cabała et al. 2004a, b). In twentieth century, intense development of the industry caused the rapid increase of anthropogenic pressure. In the vicinity of the study area, many mines, smelters, power plants, and cement mills were built, and at present, they are the sources of industrial dusts that contaminate the soil with numerous pollutants.

2.3 Geological background

The study area was mostly created of Cambrian, Ordovician, and Silurian formations covered with Devonian and Carboniferous carbonaceous formations, sands, and loamy sands. The occurrence of Pb and Zn ores was mostly related to the ore-bearing dolomites that were deposited in irregular layers of carbonaceous Triassic formations (Cabała 2009; Górecka 1993).

Ores deposited in the study area were the part of the Silesian–Cracow ore deposits and were classified of Mississippi Valley type, accordingly to their mineral composition (Viets et al. 1996; Cabała et al. 2008; Cabała 2009). The most common forms of Pb and Zn in ores were sulfides. Additionally, also carbonates of Pb and Zn were found in ores, and accordingly, the occurrence of ores deposits was strongly related with the presence of ore-rich dolomites. Previous study (Cabała et al. 2004a, b) showed that high content of Zn in ores, but also in soil, was strongly related to the high content of Pb. Moreover, sulfides of Cd were also found in ores and similarly high content of As was common in ores of the study area. Their occurrence was mostly related to the presence of marcasite and pyrite (Cabała 2001). In the study area, maximum observed concentrations of As, Cd, Pb, and Zn were very high, reaching over 10,000 mg/kg in some locations.

Pb- and Zn-enriched ores were locally deposited on very shallow depths due to the geological composition and formation of the bedrock that took place in Triassic age. As a result, ores were exposed to the hypergenic factors that increased the migration of Pb and Zn through the vertical profile. The mobilization of these metals was connected

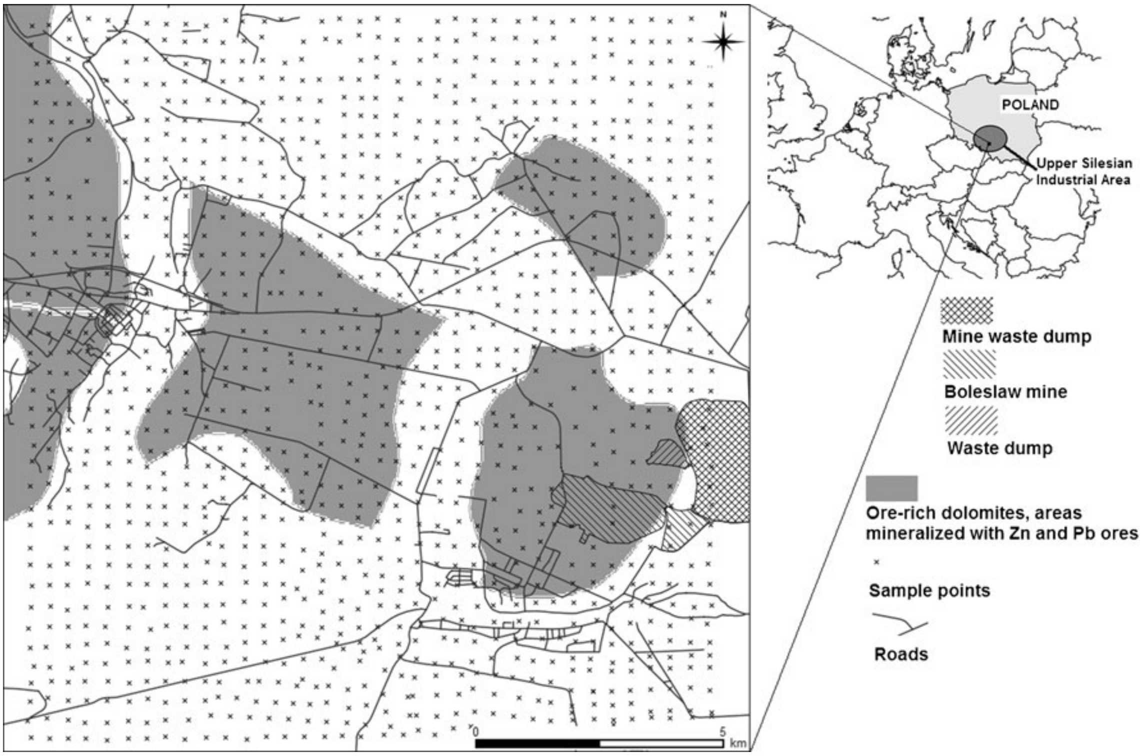

Fig. 1 Location of study area and points of soil core sampling. The areas mineralized with ores rich in Zn and Pb were denoted in *gray*

with reactions of Fe, Zn, and Pb sulfides, which was mostly observed in areas with the presence of ore-rich dolomites (Cabała 1995). In the direct vicinity of the fault zones, collapse breccia, erosion gaps, and karstic caverns, ore deposits were the most exposed to hypergenic factors causing the oxidation of ores (Cabała 2001). As a result, heightened concentration of Pb and Zn, resulting from lithogenic origin, was observed not only in parent bedrock, but also in soil (Żabiński 1964; Radwanek-Bąk 1983; Cabała 1987; Mayer et al. 2001; Trafas et al. 2006). Such effect was observed as aureoles of Pb and Zn concentration in soil (Cabała 2009; Mayer et al. 2001).

Apart from the natural lithogenic concentration of the Pb and Zn, soils were also exposed to the serious anthropogenic pressure, which was mostly associated with a mining activity in the study area. Consecutively, soils were highly degradated and at some locations, especially near Bolesław mine, the soil was almost completely removed, and only initial or industrial soils were present.

3 Materials and methods

3.1 Sampling and chemical analyses

The entire study area was sampled using regular grid with an average distance of about 250 m between sample points equally distributed. As a result, over 1,000 60-cm-long soil cores were sampled using a steel probe and plastic tubes with a diameter of 8 cm. After, cores were transported to the laboratory and divided into two subsamples covering the layers from 0 to 20 cm (layer 1) and from 40 to 60 cm (layer 2).

Particular soil samples were digested using HCl and heated at the temperature of 90 °C for 1 h. After that, 100-ml samples were used to determine the concentration of individual metals (As, Cd, Pb, and Zn) by inductively coupled plasma mass spectrometry, using the spectrometer Philips PV 8060. All field measurements and subsequent laboratory measurements were the part of the national large-scale soil inventory, covering the entire area of Poland, performed by Polish Geological Institute in the 1990s of twentieth century. The study area, because of its significance, was sampled about four times denser than the rest of the country (Lis and Pasieczna 1999).

3.2 Statistical and geostatistical methods

Statistical analyses carried out in Statistica software included calculation of selected descriptive statistics and selected statistical tests used for comparing chemical concentrations. Average concentrations of particular heavy metals were tested using transformed distributions of As, Cd, Pb, and Zn because of the violation of the normal distribution assumption of the input data. *T* test or Satterwhite test was used at the confidence level of α=0.05, depending on the equality or inequality of the variances.

All spatial distributions of metals in soil were estimated using ordinary kriging (Goovaerts 1997; Isaaks and Srivastava 1989). Concentrations were estimated using values measured in sample points multiplied by kriging weights. Kriging weights were calculated using previously calculated and modeled variograms. Data handling and presentation were made using free softwares QGIS and SAGA for geostatistical calculations.

4 Results and discussion

Maximum concentrations of Pb and Zn in soil in study area were very high, reaching 24,000 and 77,000 mg/kg, respectively (Table 1). High concentrations of Pb and Zn, but also of other metals, were often found in the previous studies related to the USIR (Cabała et al. 2004b; Cabała 2001; Lis and Pasieczna 1999).

Similarly, maximum concentrations of As and Cd were also very high, reaching about 1,000 mg/kg. Those maximum values were, in most cases, observed in the direct vicinity of the Bolesław mine and its dumps, where the anthropogenic pressure was very high. Average concentrations were also high (see Table 1). All distributions were characterized by strong skewness because of the significant number of extreme values observed near Bolesław mine.

Average Zn concentration in soil in area with ore-bearing dolomites was about three times higher than Zn concentration in the remaining part of the study area. This was observed on both layers in soil profile, down to 20 cm, and from 40 to 60 cm below the soil surface. Such results are consistent with the high content of Zn in ores that are common in this area (Cabała 2009).

High differences were observed for Pb mean concentrations on the deeper layers in the soil profile. In the upper layer, the differences in mean Pb concentrations were statistically significant (see Table 1). Analogous situation was observed in case of mean Cd concentration on the layer 2, but on the layer 1, Cd concentrations were more alike. Only in case of concentrations of As, both in areas with and without ore-bearing dolomites, means were comparable and did not differed significantly.

For all studies metals, but especially for Pb and Zn, very high differences between minimum and maximum values were observed. Such differences were the result of the two factors. First one was associated with the fact that the study area encompassed the variety of types of land management. In the area of the mines and their dumps, extreme concentrations were observed while in forest they were very low. The second factor was associated with high concentration of Pb and Zn minerals in ores.

In order to investigate the aureoles of As, Cd, Pb, and Zn concentration in soil, spatial distributions were calculated using ordinary kriging. For As, Cd, Pb, and Zn concentration in soil on both layers, contours were made with intervals of 100, 100, 2,000, and 5,000 mg/kg, respectively. Delineated aureoles of As, Cd, Pb, and Zn were presented in Figs. 2 and 3.

Table 1 Descriptive statistics and the comparison between average As, Cd, Pb, and Zn concentrations in soil with and without ore-bearing dolomites on layers 1 and 2

Layer	Type			As	Cd	Pb	Zn
1	Dolomites	Average	[mg/kg]	60	15	368	1,994
		Median		17	2	60	273
		Min		5	0.5	5	12
		Max		1,330	746	24,043	66,658
	Other locations	Average	[mg/kg]	56	9	192	444
		Median		10	1	14	30
		Min		5	0.5	5	5
		Max		1,282	256	20,597	51,966
Statistical test				–	–	+	+
2	Dolomites	Average	[mg/kg]	41	13	408	1,934
		Median		18	5	182	564
		Min		5	0.5	7	35
		Max		1,031	574	16,828	77,134
	Other locations	Average	[mg/kg]	32	5	203	515
		Median		9	2	66	124
		Min		5	0.5	5	4
		Max		1,083	194	16,637	45,295
Statistical test				–	+	+	+

"+" and "–" denote that the difference between averages was and was not statistically significant (α=0.05), respectively

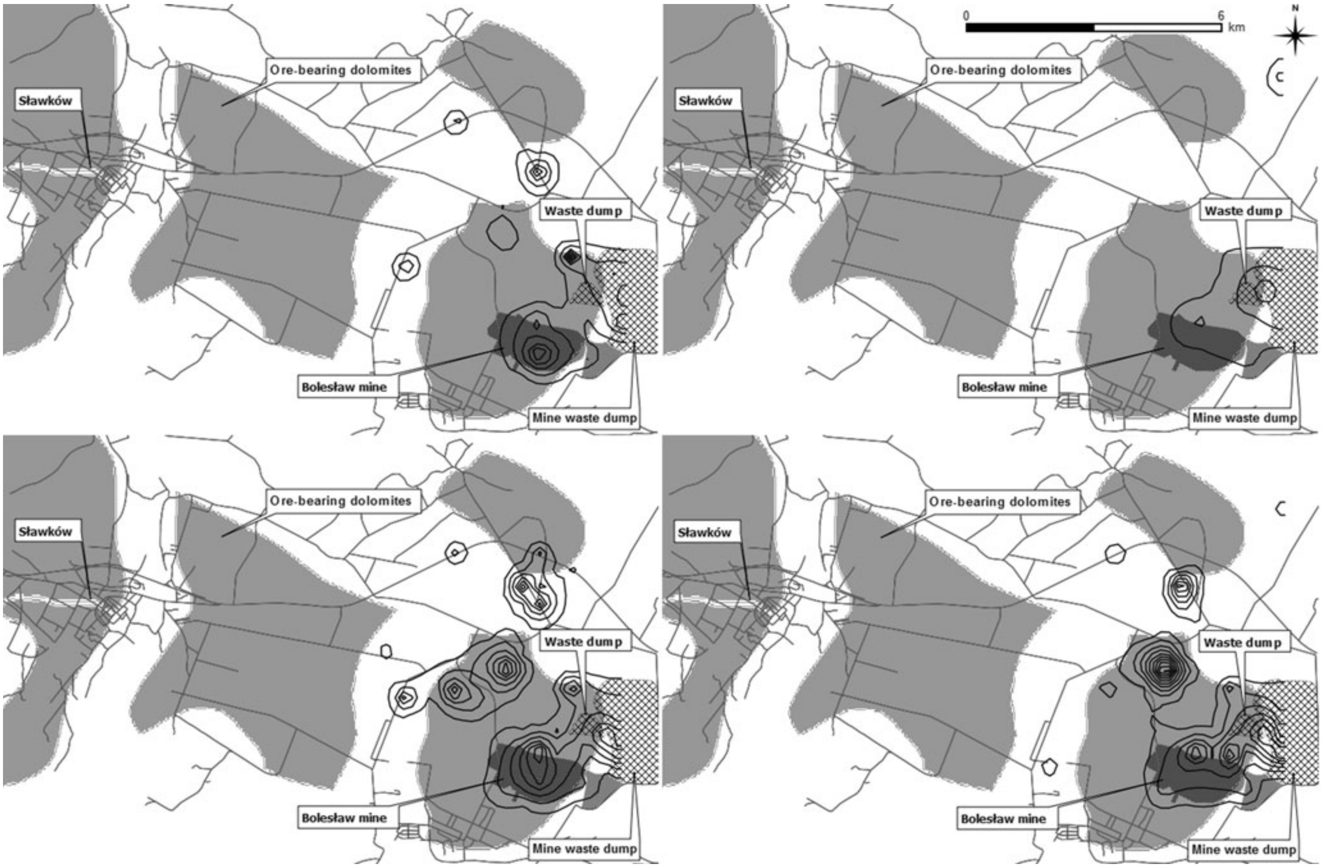

Fig. 2 Aureoles of Pb (*upper row*) and Zn (*lower row*) concentration in soil on the layer 1 (*left pictures*) and the layer 2 (*right pictures*); isoline intervals are equal, 2,000 mg/kg for Pb and 5,000 mg/kg for Zn

Almost all of the aureoles of all investigated metals were found in area with shallowly deposited ore-bearing dolomites. In the area not covered by the range of the presence of ores, aureoles of Pb and Zn were not observed with the exception of several minor ones (see Fig. 2).

The largest Pb and Zn aureoles were observed in the vicinity of Bolesław mine and nearby mine waste dump. In this location, high anthropogenic pressure enhanced significantly the effect of aureoles resulting from the shallowly deposited ore-bearing dolomites. Aureoles of Pb for the layers 1 and 2 revealed significant dependence, considering both their location and the shape. Such similarity observed on depths down to 60 cm suggests that aureoles located in the area of mine waste dump were the result of high quantity of deposited mining wastes exposed to the long-lasting hypergenic factors. This caused the migration of Pb and Zn down to the lowest of investigated depths. According to the observed extreme concentrations of Pb and Zn, it can be assumed that, in this location, the anthropogenic factor was predominating the lithogenic one, demonstrated by high concentration of Pb and Zn in ores. The impact of the shallowly deposited ore-bearing dolomites was a minor factor influencing observed aureoles in the vicinity of Bolesław mine.

Several small aureoles of Pb concentration on the layer 1 were only observed in the north 2 to 3 km away from Bolesław mine that were not present on the layer 2. This can be a result of the local anthropogenic pollution that reached upper soil layers only. Moreover, those aureoles were not located in the area with shallowly deposited dolomites (see Fig. 2).

Zn aureoles revealed similar spatial pattern to the Pb aureoles. They were observed mostly in the vicinity of Bolesław mine and its mine waste dump. Two aureoles were observed about 2.5 km away from the Bolesław mine (in the north). The aureole for the layer 2 was less distinct but has very similar shape to the aureole observed for layer 1. The location of those aureoles, near Boleslaw mine, suggests that anthropogenic influence was strongly pronounced. However, as it was previously suggested in the literature (Cabała 2009), hypergenic factor lasting over long period of time may cause that heightened Pb concentrations may be observed in upper soil layers, located above those rich in ores. The fact that aureoles of Pb were observed regularly on the layers 1 and 2 may suggest that those aureoles were related to the presence of ore-bearing dolomites.

Location, shape, and spatial pattern of Cd aureoles, especially those calculated for depths down to 20 cm below

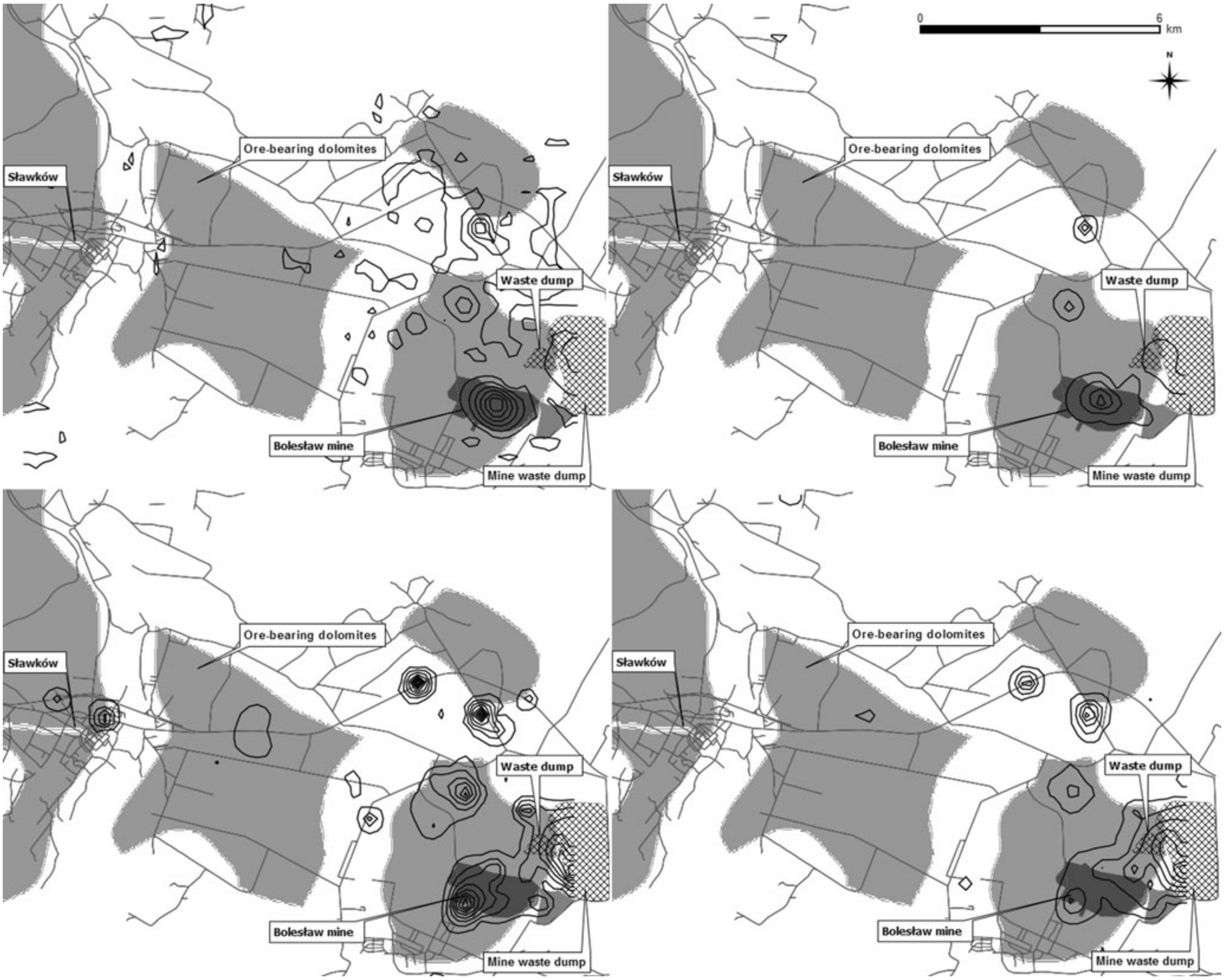

Fig. 3 Aureoles of As (*upper row*) and Cd (*lower row*) concentration in soil on the layer 1 (*left pictures*) and the layer 2 (*right pictures*); isoline intervals are equal, 100 mg/kg for As and Cd

soil surface, were weakly correlated with the location of shallowly deposited ore-bearing dolomites. Aureoles, rather faintly visible, were dispersed in the eastern part of the study area. This observation may be a result of the rather homogeneous spatial distribution of Cd concentration in soil. Moreover, Cd aureoles on the depth between 40 and 60 cm were observed only in the direct vicinity of the mine, probably suggesting that the concentration of Cd in the study area was mostly influenced by anthropogenic pollution, instead of the natural concentration of Cd in ore-bearing dolomites.

Aureoles of As were characterized by spatial pattern very similar to the aureoles of Pb and Zn. This was observed both on the layer 1 and the layer 2. Such observation may suggest that, firstly, aureoles observed near mine waste dumps were rather dominated by the anthropogenic pressure, while the remaining ones were likely influenced by shallowly deposited ore-bearing dolomites. As it can be found in previous studies (Cabała 2009), apart from above described aureoles, two small ones were located in the area in the south from the Bolesław mine. As it was studied before, this area was characterized by high concentrations of Tl (Lis and Pasieczna 1999), and high concentrations of As and Tl were found to be correlated (Cabała 2009; Dmowski and Badurek 2002). Small aureoles of As were also observed in the center of the study area and in the vicinity of the Sławków town, located in the western part of the study area.

All aureoles located within the direct vicinity of Bolesław mine and its waste dump were mostly influenced by anthropogenic factors associated with mining activities, long-lasting deposition of mine wastes, and hypergenic factors causing migration of metals through the soil profile. Anthropogenic pollution was enhancing and, in some part, masking the influence of the shallowly deposited ores.

5 Conclusions

The majority of the aureoles of As, Cd, Pb, and Zn were located within the direct vicinity of the Boleslaw mine, which may suggest high anthropogenic influence on the observed aureoles. However, neighboring area of the mine was also rich in Pb and Zn ores, and almost all dispersion aureoles of Pb and Zn were located at those locations where ore-bearing dolomites were deposited. Consequently, the aureoles of Pb and Zn were associated with a mineral composition of those ores.

The spatial pattern of the As and Cd aureoles was different from that for Pb and Zn. Major aureole of Cd was located within the mine complex, and it is probable that the anthropogenic factor was strongly predominant than the lithogenic one. In the areas located farther from mine, Cd spatial distribution was rather homogeneous and no aureoles were observed.

The origin of aureoles of As can be classified as both anthropogenic and lithogenic. The first case is associated with the aureole located near the mine, and the second one with aureoles observed in locations where, as it was previously studied, high Tl concentrations were found.

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